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**ATOMIC FORCE MICROSCOPE  
BASED ANALYSIS OF BOUND AND  
BOUND + MOBILE PHASE  
MONOLAYER BEHAVIOR UNDER  
MECHANICAL AND ELECTRICAL  
STRESS**



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<b>ABSTRACT (Maximum 200 Words), ,</b> One of the major problems with microelectromechanical systems (MEMS) is the stiction caused by capillary, van der Waals, electrostatic, and chemical forces. Self-assembled monolayers are extensively used to resolve this problem and they have been effective to a certain extent. It has been noted that the molecular weight, entanglement of molecules with asperities, time dependent interactions between asperities and monolayers, and surface migration play major roles in the failure of these coatings. In addition, tribological stressing and diffusion at increased in the failure of these coatings. In addition, tribological stressing and diffusion at increased temperature can also cause monolayers to fail. In this study, atomic force microscopy (AFM) and related techniques are used to analyze the behavior of bound monolayer films of 1-decanol and bound 1-decanol combined with a mobile phase (a pentaerythritol ester). Molecular reorientation and surface detachment under electrostatic force increase with increasing electric field between the AFM tip and the film.					
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# Atomic force microscope based analysis of bound and bound+mobile phase monolayer behavior under mechanical and electrical stress

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One of the major problems with microelectromechanical systems (MEMS) is the stiction caused by capillary, van der Waals, electrostatic, and chemical forces. Self-assembled monolayers are extensively used to resolve this problem and they have been effective to a certain extent. It has been noted that the molecular weight, entanglement of molecules with asperities, time dependent interactions between asperities and monolayers, and surface migration play major roles in the failure of these coatings. In addition, tribological stressing and diffusion at increased temperature can also cause monolayers to fail. In this study, atomic force microscopy (AFM) and related techniques are used to analyze the behavior of bound monolayer films of 1-decanol and bound 1-decanol combined with a mobile phase (a pentaerythritol ester). Molecular reorientation and surface detachment under electrostatic force increase with increasing electric field between the AFM tip and the film. The AFM tip is used as a single asperity contact to study the atomic scale film failure dynamics of MEMS materials. The micronanotribology of both bound and bound/mobile systems show significant differences in tribochemistry and replenishing characteristics. Bound and mobile phase films exhibit desirable tribological characteristics that extend the reliable life of MEMS devices, which is demonstrated in real device tests. © 2004 American Vacuum Society. [DOI: 10.1116/1.1787517]

## I. INTRODUCTION

Microelectromechanical system (MEMS) devices have potential for use in advanced technological systems like satellites, aircraft, medical devices, and automobiles. The performance of MEMS is often degraded due to the unstable interfaces of contacting surfaces and underdeveloped methods of controlling the instability. A variety of surface modification methods have been developed to overcome the interface instability. One of the effective methods is the deposition of self-assembled monolayers with various backbone chain lengths and functional groups. Various research groups have studied self-assembled monolayers derived from alkyltrichlorosilanes, specifically octadecyltrichlorosilane and 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane deposited on Si.<sup>1-3</sup> Alkane based coatings provided antistiction capabilities that are comparable to that of silanes.<sup>4</sup> A load dependent crystalline ordering was observed by Salmeron and co-workers in their atomic force microscope study of alkanethiols on gold and alkylsilanes on mica.<sup>5</sup> In grazing angle x-ray studies of similar films, it was shown that the relative lengths of monolayer chains can control interface properties to a large extent.<sup>6</sup> Microscale friction measured on molecules terminated with different functional groups were studied in detail and larger functional groups increase the friction due to increased steric interaction that increases energy dissipation.<sup>7</sup> A comparative study of the effectiveness of chain length in controlling the nanoscale friction has been studied by a number of groups. A decrease in friction with increased chain length has been generally observed from all

these studies.<sup>8-11</sup> But in the case of dialkyl sulphide monolayers on gold, an increase in friction with chain length was reported when scanned with functionalized tips.<sup>12</sup> The contrasting result for these monolayers was attributed to chain interdigitation at the molecular level.

Even though all these coatings control surface forces to varying degrees, prolonged use wears off coatings and exposes the silicon surface, which leads to adverse tribochemical changes to the interface. To ensure the prolonged life of MEMS, chemically bound layers may be supplemented with lubricious mobile species that can replenish and protect the interface from wear.<sup>13</sup> It has been observed in the case of perfluoropolyether applied on silicon that the mobile phase can replenish the tribological interface when an optimum ratio of chemically bonded (bound) and physically adsorbed (unbound) molecules are deposited.<sup>14</sup> Bound and mobile phase Zdol® was successfully applied as lubricating system in the case of microelectromechanical systems.<sup>15</sup> However, the statistical distribution of performance was not satisfactory probably due to the nonuniformity of the Zdol coating. Alkane molecular chains covalently bonded to diamond were modeled using classical molecular dynamics and it was shown that friction is dependant on packing density when sliding occurs under varied stress levels.<sup>16</sup> Our recent studies show that hydrocarbon molecules with hydroxyl functional groups (1-decanol) provide some lubricity when applied as a bound phase to silicon surface, but significant increase in wear life could be observed when a mobile phase (ester) was added to the bound layer to provide replenishment.<sup>17</sup> The mechanisms responsible for the substantial increase in wear life prompted further study of this material system at a basic level.

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In this study, the behavior of 1-decanol films alone and combined with a mobile phase are compared in low load contact scans under normal atmospheric conditions and in an atmosphere devoid of oxygen and humidity (i.e., dry nitrogen). A contact and tapping mode atomic force microscopy (AFM) capable of nanolithographic patterning was used for this purpose. The significance of this setup is that an area that has been scanned in contact mode can be imaged in non contact mode without changing tip or scanning head enabling visualization of the tribological change that occurred during the contact scan. The biased AFM tip is used as a single asperity interface that imparts electrical and mechanical stress to the films and is also used to image the changes occurring under stress. Nanolithography derived techniques are used here to form small structures and microscopic discontinuities (nanocuts) and to monitor the migration and adhesion characteristics of resulting structures.

## II. EXPERIMENT

Si (100) wafers were first subjected to ultrasonic cleaning separately in hexane, acetone and methanol for 30 min each, and dried. The wafers were treated with 52% aqueous hydrofluoric acid for 2 min and washed thrice, 5 min each, with methanol. The freshly treated wafers having mostly Si-H surface groups were dip-coated in a 0.2% (w/v) solution of 1-decanol in hexane. Dip coating was conducted by immersing the wafers at a rate of 1.0 mm/s into the coating solution using a motorized device. The wafers were kept immersed in the solution for 1 min and were withdrawn at the same rate. The coated wafers were then heated at 90 °C for 1 h to bind the alcohol unit to the silicon surface as shown below



Covalent bond formation between freshly etched silicon and alcohols under these conditions have been reported earlier.<sup>18</sup> After cooling, the wafer was treated with methanol thrice (5 min each), in an attempt to remove unbound alcohol. Where applicable, the mobile phase, pentaerythritol tetraheptanoate  $\{\text{C}[\text{CH}_2\text{OC}(\text{O})(\text{CH}_2)_5\text{CH}_3]_4\}$ , was applied by dip coating as before from a 0.2% solution in hexane. After coating with the mobile component, the wafers were not washed or heated, but allowed to dry in air, and stored in a glass jar closed with aluminum-lined plastic stoppers for testing.

A Dimension 3100 with Nanoscope IV controller by Digital Instruments was used in this study. This instrument was capable of making contact and tapping mode (intermittent contact mode) scans without changing either tip or scanning head. This allows the user to monitor the changes in topography caused by the contact scan without further disturbance from the contacting tips. In contact mode, the AFM tip touches the surface while in noncontact mode it vibrates in a forced mode frequency at a certain height. The variations in the amplitude of vibrations caused by the proximity of surface structures are monitored to form topography images of

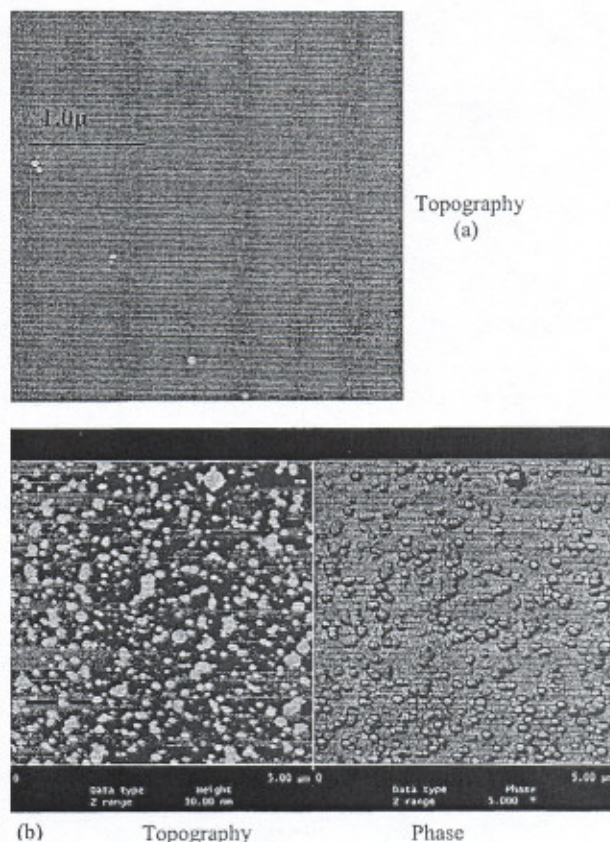


FIG. 1. (a) Topography of a 1-decanol coated silicon wafer shown by a 2.8  $\mu$  tapping mode scan. (b) Topography and phase image of an aggregated film of 1-decanol on silicon shown by a 5  $\mu$  tapping mode scan.

the surface under study. The time lag in the variation of the oscillation caused by the proximity of surface structures depends on the chemical nature, mechanical stiffness, and adhesive nature of these structures. The lag can be monitored as a phase shift between the driving frequency and the actual frequency of the probe and is recorded at each pixel. Pixel brightness is set to vary according to the phase shift and interpreted as the phase scan image. Since the phase shift caused by loose structures is larger than stable bound structures, contrast variation in a phase scan is a good measure of structure strength, adhesion and chemical bond strengths.

## III. RESULTS AND DISCUSSION

### A. Characteristics of surfaces coated with bound phase only

Figures 1(a) and 1(b) show topography of 0.2% decanol film formed on a silicon surface. The average roughness of this surface is 0.2 nm on a  $1 \times 1 \mu\text{m}^2$  area base and peak to valley height variation is 2.6 nm. Figure 1(a) is a uniformly coated surface without much loose unreacted species. The island like structures in the topography in Fig. 1(b) might have been caused by condensation of loose unreacted species. The islands are of 100–200 nm of average diameter and 4–20 nm in height. Aggregation and island formation in



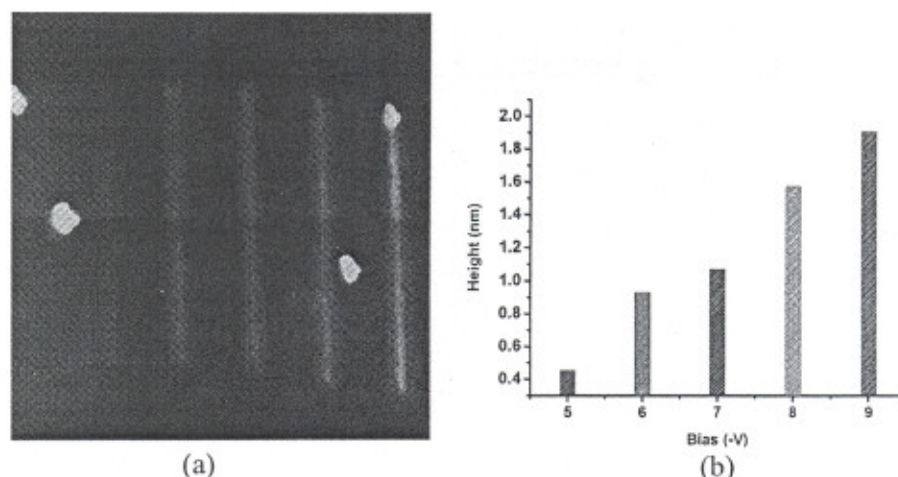


FIG. 2. (a) Topography of lines drawn with an AFM tip at a steady height biased with different negative bias shown by a 5  $\mu$ m tapping mode scan. (b) Height variation of wedges formed with bias.

monolayers films have been reported earlier for perfluorodecyltrichlorosilane (FDTs) films.<sup>19</sup> In this case, islands were more pronounced and more separated than our case. It was noted that aggregate formation could reduce the usefulness of FDTs films in controlling stiction in MEMS. The phase contrast variation between the rim and the inner regions of the islands in Fig. 1(b) implies that the rim of each island is bound or strongly attached, while the inner region is composed softer, less adhesive structures. These softer structures may be composed of entangled loose molecules.

Figure 2(a) shows wedge shaped lines drawn by an AFM tip biased at various negative bias. The tip was moved 0.175  $\mu$ m/s at about 50 nm above the surface. The wedge height variation with bias is shown in Fig. 2(b). The reorientation of 1-decanol molecules coupled with silicon oxidation due to the electrostatic field from the biased tip may have caused the wedge formation. Under similar conditions, a high electrostatic field can oxidize an exposed Si surface.<sup>20</sup> Nanoscale oxidation of Si surfaces by biased atomic force microscope tips has been observed by a number of authors.<sup>21–24</sup> A detailed quantitative study for this process has been reported for different biasing conditions and surrounding humidity.<sup>25</sup> The rate of oxidation and the oxide volume generated at various currents and biasing conditions were also evaluated in that study. Comparing the oxide volume generated in the referenced study under similar conditions to ours shows that the volume generated in our wedge-like lines is far greater than that for the bare silicon. The excess volume is likely due to the presence of monolayer film. It is likely to have been caused by the oxidation of attached 1-decanol chains or reorientation of 1-decanol molecules that are still left unattached to the Si surface, aligned or condensed under the strong electrostatic force from the negatively biased tip traveling at close proximity. The polar nature of these unattached 1-decanol molecules may allow these molecules to align with the electric field.

Similar protrusions of polymer thin films under biased atomic force microscope tips have been observed by other

authors.<sup>26</sup> In that study, the movement of the attached polar functional groups in the direction of the electric field was assisted by increased mobility due to elevated temperature. In our study, wedges were formed only for bias of -5 to -9 V, which was the limit of the instrumentation. Below -5 V, no wedges were observed.

Figure 3(a) shows the reorientation of molecules under a constant negative bias (-9 V) with varying tip proximity to the surface. The wedge height increases linearly until the tip is very close to the surface [Fig. 3(b)]. After a certain approach distance, the wedge height began to diminish. This is probably caused by the dissipation of electric field as the tip begins to touch the surface.

Figure 4 shows the topography and phase image of a bound phase (1-decanol) film after contact scanning with an uncoated Si AFM tip at 50 nN normal load under humid (40%–45%) ambient conditions. The central  $1 \times 1 \mu\text{m}^2$  area is covered with irregular protrusions that resulted from contact scanning. The average height of these structures is 40.1 nm and the roughness was 7.9 nm. The scanning creates a large amount of wear debris that is seen as irregular islands in the scanned region. The significance of phase contrast in scanning probe microscope is still under debate within the AFM community. However, the most accepted interpretation of phase shift origination is that it is due to the difference in energy dissipation between phase contrasting areas.<sup>27,28</sup> The low contrast in the phase mode image suggests that these "third bodies" have similar energy absorption characteristics to that of the surroundings showing their lack of freedom for vibration or their binding to the surface.

To study the diffusion of these structures, the area was left undisturbed and scanned again after 20–25 min. No significant changes were observed both in topography and phase mode images in later scans suggesting the immobile and passive nature of these structures to surroundings and humidity.

In order to understand the mobility of these structures, the AFM tip was used to separate the structures by dragging the tip through the wear debris. Figure 5(a) shows the topogra-



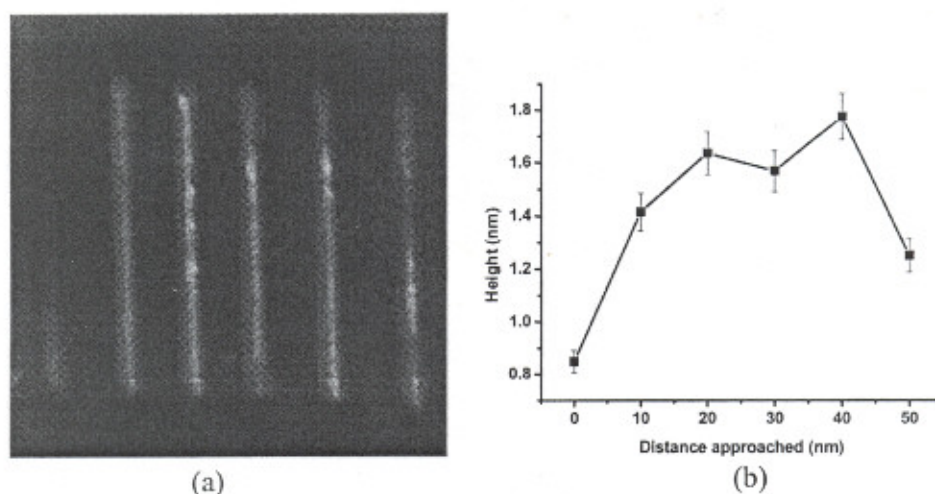


FIG. 3. (a) Topography of lines drawn with an AFM tip biased at 9 V at different proximity shown by a 5  $\mu$  tapping mode scan. (b) Height variation of wedges formed with tip heights.

phy after a line was drawn through the wear debris with a lighter normal load (100 nN) and the line was barely seen. When the force was increased to the 150 nN range, the debris moved and clearly showed the path of the AFM tip [Fig. 5(b)]. Further scans of this area did not show any change in the wear debris distribution even though they were disturbed from their original locations by the AFM tip, which implies that there are no additional unbound (or less tightly bound) pieces produced from AFM tip movement.

To further understand the tribochemistry of these structures, similar scans were made after filling the chamber with dry nitrogen. The system was flushed overnight and a steady value of zero humidity was obtained. Figure 6 shows the comparison of topographies obtained from contact scans with similar contact forces but different surrounding gases. Figure 6(a) shows the topography formed in air with 50% humidity and Fig. 6(b) shows the topography obtained in dry nitrogen. The  $1 \times 1 \mu\text{m}^2$  area contact scanned under humid-

air generates thick wear debris attached together to form large crystal-like structures with sharp edges. From close examination of this debris, the repeated occurrence of a particular shape for these crystallites was probably caused by the "tip effect" (some tiny crystallite adhered to the tip so that its scanning cross section is changed to the cross section of the crystallite).

The approximate roughness and peak to valley height variation is 6.0 and 37.2 nm, respectively. However, the area scanned in dry nitrogen shows substantially different topography with little buildup of wear debris. The structures formed here are more round shaped and much smaller in size. The average roughness and peak to valley height variation is 0.21 and 1.9 nm, respectively. It is very clear that air and humidity cause a large quantity of wear debris while dry nitrogen helps to minimize wear debris. There are two significant differences in these cases. When water is present in the surroundings, the normal load may be increased due to a

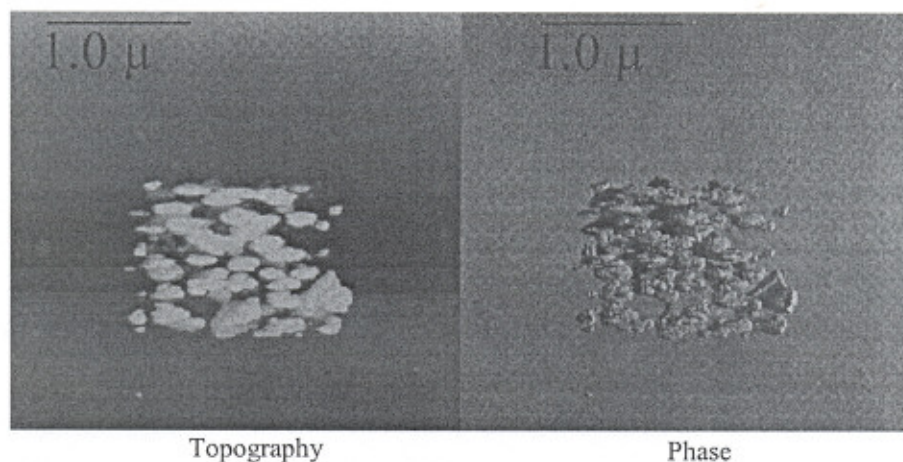


FIG. 4. Topography and phase image shown by a 3  $\mu$  tapping mode scan of 1-decanol on silicon after  $1 \times 1 \mu\text{m}^2$  contact scan with 100 nN normal load.

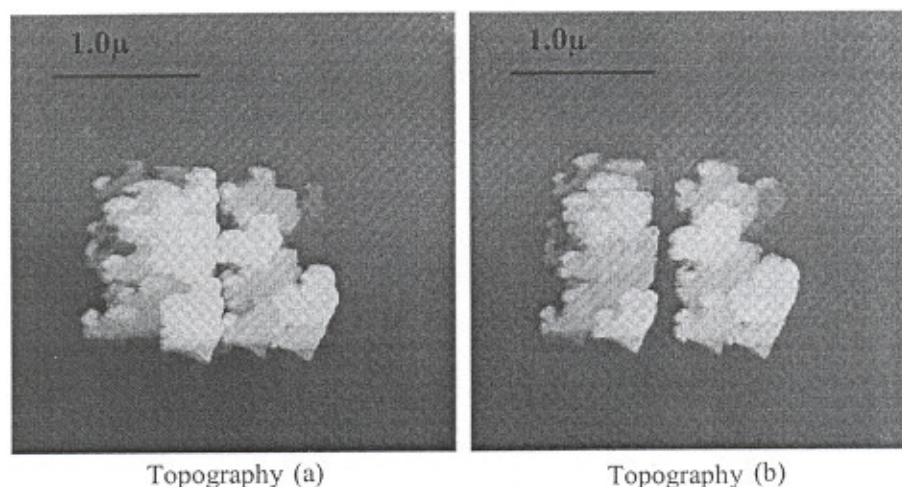


FIG. 5. (a) Topography shown by a  $3\ \mu$  tapping mode scan after a line was drawn with an AFM tip through wear debris with a lighter normal load (100 nN). (b) The topography shown by a  $3\ \mu$  tapping mode scan when the normal load was increased to 150 nN.

water meniscus and the increased rate of oxidation due to wet oxidation of Si. It has been established that wet oxidation of Si is much faster than dry oxidation.<sup>29,30</sup> In addition, the presence of water vapor makes the formation of oxide much easier due to the increased contact load, which leads to the exposure of more Si atoms. From this, it is implied that the wear debris formed might be third bodies resulting from the oxidation of exposed Si and the combination of aggregated monolayers combined with  $\text{SiO}_x$ ,  $\text{SiO}_2$  crystals.

#### B. Characteristics of surfaces coated with mobile and bound phase

The topography of a film containing bound and mobile phases is shown in Fig. 7. There is no notable change in the topography of this from that of films with bound phase only.

The average roughness and peak to valley height is 0.05 and 0.35 nm, respectively. Since the mobile phase can spread over the surface, it is expected to shield the surface from adverse tribochemical reactions even when the surroundings contain reactive gases. In addition, the replenishing nature of this film helps reform the coating quickly enough to regulate direct contact of asperities with the exposed counterpart.

Figure 8(a) shows the topography of a surface coated with bound and mobile phase after contact scanning in air with 50% humidity. The wear debris formed in this case is like islands with no sharp corners signifying the surface energy dependence of these structures. The fluid nature of these structures is further revealed when dragging the tip across one and cuts the structure. Figure 8(b) shows the topography after the cut and the resultant shapes of the separated struc-

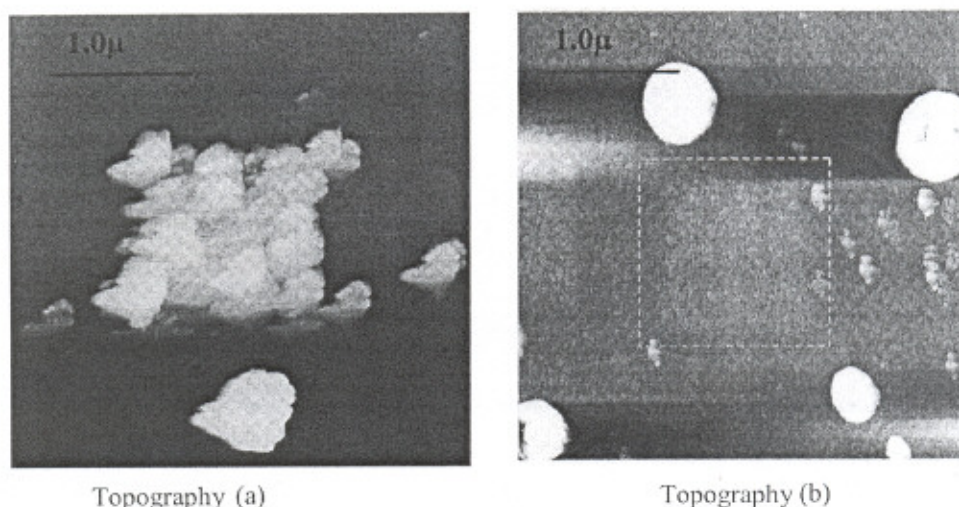
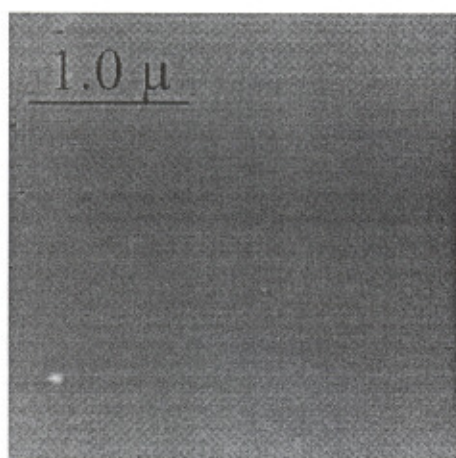


FIG. 6. (a) Topography shown by a  $3\ \mu$  tapping mode scan when RH is increased to 50% and keeping all other variables the same as in Fig. 4. (b) The topography shown by a  $3\ \mu$  tapping mode scan for  $1 \times 1\ \mu\text{m}^2$  area (dotted square), which was scanned in contact mode in dry nitrogen.





Topography

FIG. 7. Topography of a film containing bound and mobile phase shown by a 3  $\mu$  tapping mode scan.

tures {the lower big island [see Fig. 8(a)] is cut by a line drawn across it}. The round shape of the separated portions shows the tendency of these structures to minimize the surface energy by reducing the surface area.

The mobility and free flowing nature of these secondary structures is revealed when they are forcefully relocated and allowed to combine with similar structures. Figures 9(a)–9(c) reveal this phenomenon since the resultant secondary films formed by contact scanning are moved by the atomic force microscope tip using lithography-based techniques. In Fig. 9(a) a line drawn from top to bottom partially moves the top island towards the bottom and the bottom one is made thicker [see Fig. 9(b)]. The topography in Fig. 9(c) results when the bottom “thicker” island is moved to the top left smaller island and allowed to combine with each other. In all these movements in 50% relative humidity (RH), the dynam-

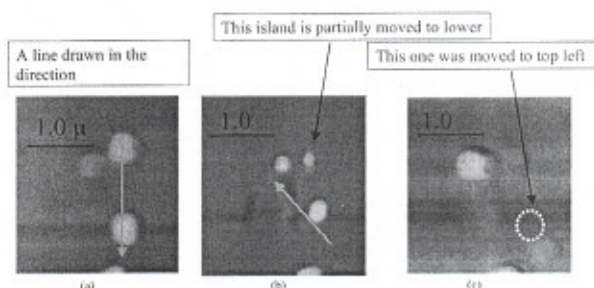
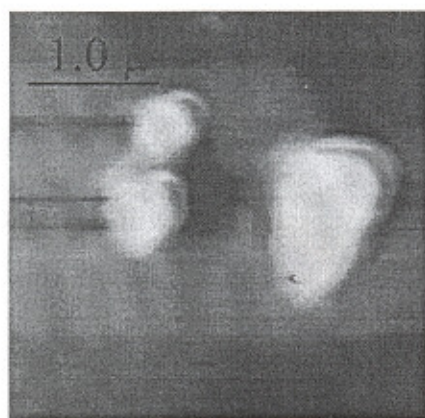


FIG. 9. (a) Topography from a 3  $\mu$  tapping mode scan before a line is drawn from top to bottom to move the top island to the bottom. (b) Topography after the line is drawn from top to bottom. (c) The topography resulting from the bottom thicker island being moved to the top left smaller island and combining together.

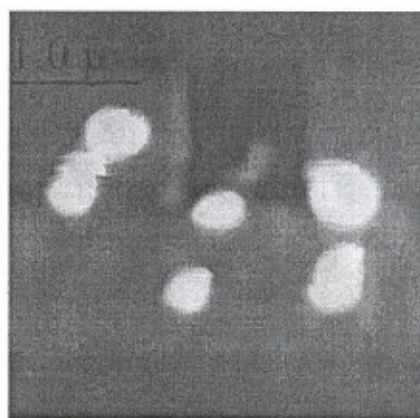
ics and steady circular shapes of the displaced structures that were created as the third bodies show that they are “liquid-like.”

It is also noted that the wear debris generated by the AFM tip in the interface of bound+mobile phase coated surfaces is significantly different in regards to mobility and replenishing characteristics when compared to that of bound phase only coated surfaces. This variation in mobility (i.e., liquid-like behavior) of wear debris makes the bound+mobile coated interface more tribologically desirable for low load applications like MEMS devices. This special coating system was applied to real MEMS devices and the wear life significantly improved when compared to uncoated devices.<sup>17</sup>

Figure 10 shows the results from the wear life study of MEMS devices with different contact interfaces. The first two bars show the average life expectancy of machines run in air with moderate humidity. The first bar is from machines with no coating and the second bar shows the average life expectancy of machines coated with bound+mobile phase films. It is evident that the coating provided a substantial increase in the wear life. The third and fourth bars show the



Topography (a)



Topography (b)

FIG. 8. (a) Topography shown by a 3  $\mu$  tapping mode scan of third bodies formed by contact scanning of a surface coated with bound and mobile phase in air with 50% humidity. (b) The topography shown by a 3  $\mu$  tapping mode scan of the resultant shapes of the separated third bodies when a line is drawn across and cuts the lower island.



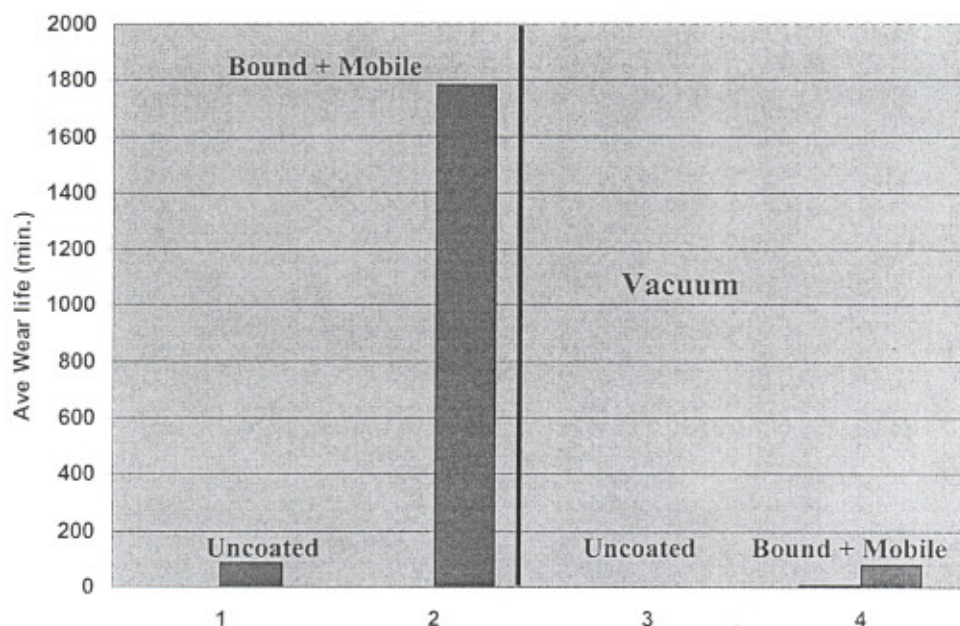


FIG. 10. Average wear life of MEMS devices with and without coating in humid air and in vacuum.

life expectancy of machines when tested in vacuum. These machines fail quite similar to uncoated machines run in humid air. However, the average wear life of coated machines in vacuum is about two orders of magnitude longer than the uncoated machines, which is around 0.9 min (not visible in the figure).

The nature of wear debris produced in a dry nitrogen atmosphere is shown in Fig. 11. The area where contact occurred is enclosed in the dotted-line square. Only small structures of wear debris were formed and they acted differently from those formed in ambient humid condition. It is

noted that there is practically no wear scar formed and the debris formed in dry nitrogen is noncircular and thereby less fluid-like (though it may be possible to impart some fluidity to this structures because of the absence of sharp corners and crystallite-like shapes). The lack of fluidity must have prevented the replenishment of the coating of the worn out regions causing the machines to fail earlier than humid conditions. For bound phase only coated surfaces there was some barely visible sharp wear debris generated in dry nitrogen which is suspected to be the conglomerates of 1-decanol mixed with loose silicon.

#### IV. CONCLUSION

Silicon surfaces coated with bound (1-decanol) and bound+mobile phases (pentaerythritol ester) were characterized using atomic force microscopy both in humid ambient and dry nitrogen surroundings. Areas scanned in contact mode were rescanned in non-contact mode to visualize the tribological changes occurring due to contact scanning. Immobile brittle bound structures were formed for bound only (1-decanol) lubricated surfaces, while flexible free flowing wear debris was generated in the case of bound+mobile lubrication. Bound+mobile lubricated surfaces resist adverse tribochemical reactions, while bound only lubricated surfaces created brittle third bodies that opposed surface modification or surface migration due to diffusion.

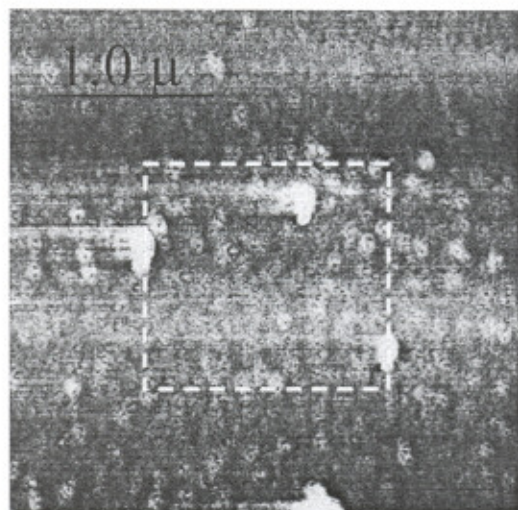


FIG. 11. Topography from a 3  $\mu$  tapping mode scan of a barely visible wear scar (dotted square) after the contact scan of bound+mobile film in dry nitrogen.

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